

Pulsed Polarization Transfer for ^{13}C NMR in Solids

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A new pulsed polarization transfer experiment method is described for the polarization of ^{13}C spins in a solid by magnetization transfer from protons. The method is directly analogous to the INEPT sequence for liquids introduced by Freeman and Morris. As polarization is transferred in PPT between individual ^1H - ^{13}C pairs, rather than between spin reservoirs, different opportunities exist for structurally selective experiments. Results on *p*-diethoxybenzene and coronene are presented.

INTRODUCTION

The routine observation of rare nuclear spins in solids, especially ^{13}C , has become feasible and popular by the use of techniques that transfer polarization from abundant spins (usually protons) to the rare spins. Various well-established methods for polarization transfer are in use. These include cross-polarization (CP) via the Hartmann-Hahn contact (1), first applied to sensitivity enhancement in the detection of ^{13}C by Pines, Gibby, and Waugh (2), adiabatic demagnetization in the rotating frame (ADRF) (3), and a method closely related to the ADRF method, but creating dipolar proton order by means of a Jeener-Broekaert 90°_x - t - 45°_y sequence applied to the protons (4, 5). Of these three approaches only cross-polarization using the Hartmann-Hahn contact can be used to full and convenient advantage under magic-angle spinning conditions, since dipolar order is destroyed by rapid sample rotation (5-7). In addition, Schaefer *et al.* (8) have shown recently that the Jeener-Broekaert sequence applied to the protons, followed by a rf field applied to the carbons for a very short period of time (corresponding to approximately a π pulse or longer), also transfers some proton polarization to the carbon-13. This experiment is referred to below as the JBSLF experiment (for Jeener-Broekaert separated local field).

All the polarization experiments mentioned above except the JBSLF experiment have the common feature that magnetization is transferred from one reservoir, consisting of proton magnetization, to the rare-spin reservoir, e.g., the ^{13}C magnetization; thus, magnetization is transferred nonselectively from a large collection of protons to a large collection of ^{13}C nuclei. Because of this reservoir-to-reservoir transfer, the experiment can advantageously be described conveniently in thermodynamic terms. This characteristic is also one of the reasons for the large sensitivity enhancement obtained by these methods. The present paper describes a new polarization transfer experiment in which the transfer takes place between individual

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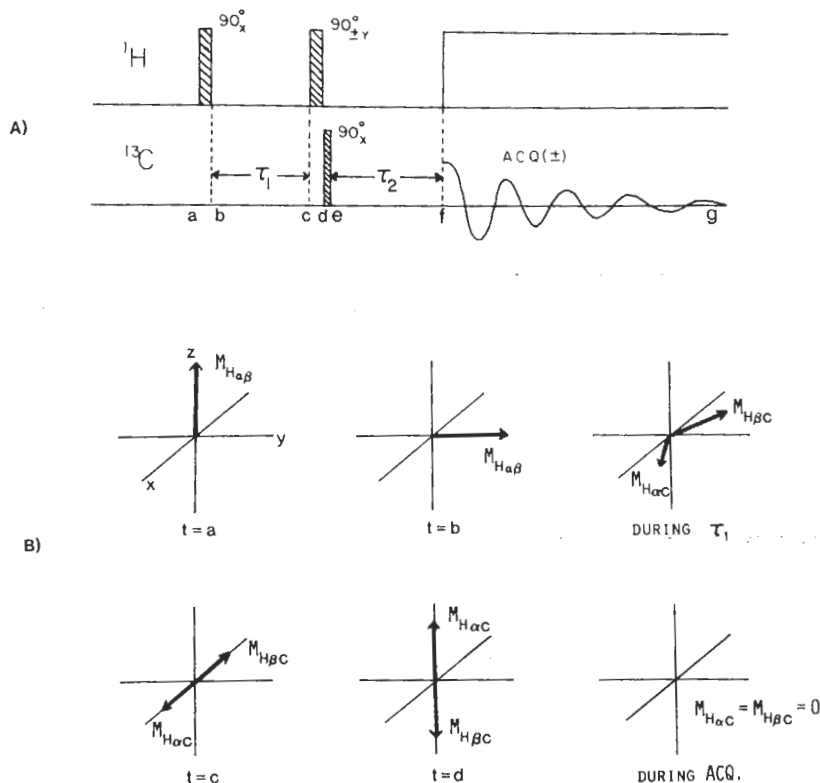


FIG. 1. A. Basic timing scheme of pulsed polarization transfer (PPT). The delays, τ_1 and τ_2 , are on the order of $10 \mu\text{sec}$. The second ^1H pulse is alternated in phase along the y axis, with data correspondingly added or subtracted in memory. B. Vector diagrams of ^1H magnetization in the PPT experiment. $M_{H\alpha\beta}$ represents the ^1H magnetization arising from ^1H - ^{13}C pairs with β ^{13}C spin states. $M_{H\alpha\alpha}$ represents ^1H magnetization from ^1H - ^{13}C pairs with α ^{13}C spin states.

nuclei, and not between the reservoirs. Because each spin reservoir does not participate collectively in this new polarization-transfer method, the experiment cannot be described by the use of thermodynamics. However, it is shown below that a vector picture, as commonly used in liquid-state NMR, is useful in describing this new experiment. The new method can be applied under magic-angle spinning conditions, as well as with a nonspinning sample. It is shown that this new experiment is closely related to the INEPT experiment introduced for polarization transfer in liquids by Freeman and Morris (9). The experiment reported here has some similarities to the JBSLF experiment, but the physical bases of the two experiments are quite different and much of the similarity is superficial.

EXPERIMENTAL

The coronene and *p*-diethoxybenzene were obtained from Aldrich Chemical Company and Chem. Services, respectively, and were used as received. The ^{13}C NMR experiments were carried out at 15.1 MHz on a home-built spectrometer, using a

FIG. 2. Population diagram between energy-level population

Varian HR-60 magnet system with a pulse width was $5 \mu\text{sec}$, that is, as described elsewhere (10).

The basic scheme of the experiment is shown in Fig. 1, which shows the magnetization transfer (Fig. 1B). To isolate ^{13}C - ^1H spin pairs, the proton chemical shift is the simple model are discussed.

After the first 90° pulse, the magnetization will start rotating about the z axis (much smaller than D , $\Delta\epsilon$) (after a period, τ_1 , follow to the α and β spin states along the y axis. These two proton magnetization vectors are shown in Fig. 1B. If τ_1 is selected so that one of the ^1H magnetization vectors is along the $+z$ axis. In this way, from Fig. 1B that the second 90° pulse (with ^{13}C in the α spin state) will transfer the magnetization associated with the $\beta^{13}\text{C}$ spin states.

The pattern of average magnetization for the four-level system is shown in Fig. 2. Examination of the $\alpha_H\alpha_C$ and $\beta_H\alpha_C$ states at equilibrium, while the relative populations of the $\alpha_H\beta_C$ and $\beta_H\beta_C$ states are inverted. Thus, the Zeeman order is transferred to the dipolar order after the second 90° pulse.

Examination of Fig. 2 shows that the ^{13}C magnetization, i.e., the $\beta_H\alpha_C$ and $\beta_H\beta_C$ states, is inverted. Hence, if a 90° ^{13}C pulse is applied, the magnetizations, $M_{C\alpha H}$ and $M_{C\beta H}$, will be inverted in opposite senses in the ^{13}C spin states.

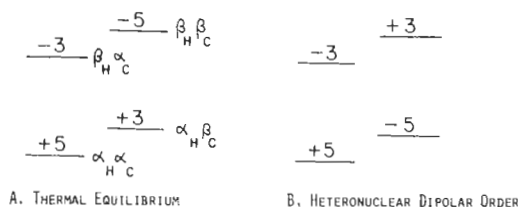


FIG. 2. Population diagram for a simple spin system consisting of ^1H - ^{13}C pairs, showing the relationship between energy-level populations and magnetizations.

Varian HR-60 magnet system and a Nicolet 1180 data system. The proton 90° pulse width was $5 \mu\text{sec}$, that of ^{13}C , $3 \mu\text{sec}$. The magic-angle spinning probe has been described elsewhere (10). Kel-F rotors, spinning at about 2.5 kHz, were employed.

The basic scheme of the pulsed polarization transfer (PPT) experiment is set out in Fig. 1, which shows the pulse sequence (Fig. 1A) and the response of ^1H magnetization (Fig. 1B). To understand the effect of this scheme, first consider a set of isolated ^{13}C - ^1H spin pairs with a time-independent dipolar interaction, D , and a proton chemical shift that corresponds to the frequency, Δ . (The limitations of this simple model are discussed briefly in the Results and Discussion section.)

After the first 90° pulse is applied to the protons (time a to b) the proton magnetization will start rotating with angular frequency $2\pi\Delta \pm \pi D$ (neglecting scalar coupling) about the z axis in the rotating proton frame (time b to c). Because Δ is much smaller than D , Δ will be neglected in the discussion that follows. At a time c (after a period, τ_1 , following the 90° pulse) the two proton vectors that correspond to the α and β spin states of the ^{13}C nucleus will be at angles $\pm\pi D\tau_1$ with the positive y axis. These two proton magnetization vectors are designated $M_{H\alpha C}$ and $M_{H\beta C}$ in Fig. 1B. If τ_1 is selected such that $D\tau_1 = 1/2$, then a second 90° pulse (at c) turns one of the ^1H magnetization components along the $-z$ axis and the other one along the $+z$ axis. In this way a state of heteronuclear dipolar order is created. One sees from Fig. 1B that the second 90° ^1H pulse places the ^1H magnetization associated with ^{13}C in the α spin state back along the $+z$ direction and the ^1H magnetization associated with the $\beta^{13}\text{C}$ state along $-z$.

The pattern of average populations of the energy levels of this simplified spin system is shown in Fig. 2 in terms of relative deviations from equal populations of all four levels. Examination of Fig. 1B for $t = d$ shows that the relative populations of the $\alpha_H\alpha_C$ and $\beta_H\alpha_C$ states, which govern $M_{H\alpha C}$, are the same at $t = d$ as at thermal equilibrium, while the relative populations of the $\alpha_H\beta_C$ and $\beta_H\beta_C$ states, which determine $M_{H\beta C}$, are inverted at time d , relative to thermal equilibrium populations. Thus, the Zeeman order of thermal equilibrium is converted to a heteronuclear dipolar order after the second 90° ^1H pulse.

Examination of Fig. 2 shows that at time d the populations that govern measurable ^{13}C magnetization, i.e., the relative populations of the $\alpha_H\alpha_C$ and $\alpha_H\beta_C$ states and the $\beta_H\alpha_C$ and $\beta_H\beta_C$ states, also have been altered relative to their thermal-equilibrium values. Hence, if a 90° ^{13}C pulse is applied (d to e), two antiparallel ^{13}C magnetizations, $M_{C\alpha H}$ and $M_{C\beta H}$, are produced in the transverse plane. These rotate in opposite senses in the ^{13}C rotating frame, and after a time, $\tau_2 = (2D)^{-1}$, these

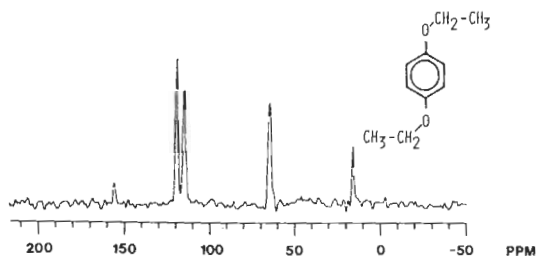


FIG. 3. Pulsed polarization transfer (PPT) ^{13}C NMR spectrum of *p*-diethoxybenzene, obtained using magic-angle spinning. The τ_1 and τ_2 delays used were 7 and 15 μsec , respectively.

magnetization vectors become parallel (at *f*). At this point ^1H decoupling is applied and ^{13}C data acquisition is carried out for the period, ACQ (*f* to *g*).

RESULTS AND DISCUSSION

In principle the PPT experiment outlined in Figs. 1 and 2 should produce a gain in ^{13}C magnetization of a factor of 4 in comparison to that available at thermal equilibrium. In addition this experiment avoids the ^{13}C spin-lattice relaxation bottleneck, because protons usually relax much faster than ^{13}C spins. Hence, this PPT experiment would appear to offer the same advantages as does cross-polarization.

In practice, of course, the situation is not as simple as sketched above. For one thing, in a polycrystalline solid the dipolar coupling, D , is a function of the orientation of the C-H internuclear vector with respect to the static magnetic field, and some kind of average value for D has to be estimated in order to set the periods, τ_1 and τ_2 . Another factor is that the two proton resonances that correspond to the α and β ^{13}C spin states are strongly broadened by proton-proton interactions, and will show severe mutual overlap. Because of proton spin diffusion this broadening is largely homogeneous and its effects are irreversible. Hence, in order to create a maximum amount of heteronuclear dipolar order, one has to set the period, τ_1 , to a value significantly shorter than the value indicated above, $(2D)^{-1}$. A typical value will be of the order of 10 μsec . The decay of the transverse ^{13}C magnetization during the time τ_2 is significantly slower than the decay of proton magnetization during τ_1 ; thus, τ_2 can be set to a value which is closer to the optimum, $\tau_2 = (2D)^{-1}$, and will be typically of the order of 20 μsec . (Considering the ^{13}C - ^1H pair as an isolated system, ^1H transverse magnetization during τ_1 suffers more dephasing from distant protons than does ^{13}C during τ_2 from its interaction with the same distant protons.) Of course, magic-angle spinning modulates the magnitude of the dipolar coupling; but this spinning is slow on the time scale in which the transfer takes place and hardly influences the results.

As the second proton pulse has a flip angle of $\pi/2$, no homonuclear proton dipolar order is created by the ^1H pulse sequence, $(\pi/2)_x - t - (\pi/2)_y$ (4). All proton multiple-quantum coherences of even orders, including zero-quantum coherence (which is not synonymous with proton dipolar order), are created by the ^1H pulse pair (11), but these are not readily transferred to single-quantum ^{13}C coherence by the $\pi/2$ ^{13}C pulse.

Figure 3 shows the PPT spectrum for *p*-diethoxybenzene, optimized with the

parameters, $\tau_1 = 7 \mu\text{sec}$ for aromatic carbons and obtained with the same mann-Hahn transfer. The spectrum (a) has a very low intensity and the relatively low intensity of the methyl intensity coupling because of the

Figure 4 shows PPT Spectrum (a) is the conventional spectrum of protonated carbons (b) shows the results of the resonance line in this spectrum. The contributions from nonprotonated carbons in the case of nonspinning ^1H pairs with small heteronuclear coupling close to the magic-angle are shown in Figs. 4b and c were 17 and 17%, respectively.

Although the ^{13}C sensitivity is less than that obtained with

FIG. 4. ^{13}C NMR spectra of *p*-diethoxybenzene obtained with MAS, obtained from the conventional spectrum (a) the PPT spectrum in the nonspinning case (b) and (c) the PPT spectrum in the nonspinning case with 17 and 25 μsec , respectively.

parameters, $\tau_1 = 7 \mu\text{sec}$, $\tau_2 = 15 \mu\text{sec}$. The signal-to-noise ratio for the protonated aromatic carbons and methylene carbons is about a factor of 2.5 less than that obtained with the same sample and spectrometer by means of an optimized Hartmann-Hahn transfer. Note that the substituted aromatic carbon resonance (at 157 ppm) has a very low intensity because of the absence of a directly coupled proton, and the relatively low intensity for the methyl carbon (at 15 ppm). The depletion of the methyl intensity is due to partial averaging of the heteronuclear dipolar coupling because of the rotation of the methyl group around its symmetry axis.

Figure 4 shows PPT spectra obtained for coronene under various conditions. Spectrum (a) is the conventional CP-MAS ^{13}C spectrum, with overlap of the resonances of protonated and nonprotonated carbons at about 120 ppm. Spectrum (b) shows the results obtained under similar conditions with the PPT sequence; the resonance line in this spectrum is considerably narrower because of the absence of contributions from nonprotonated carbons. Spectrum (c) shows the PPT result in the case of nonspinning. There is a clear dip in the anisotropy pattern due to ^{13}C - ^1H pairs with small heteronuclear interactions, i.e., with the internuclear C-H vector close to the magic-angle axis. Values of τ_1 and τ_2 used for obtaining the spectra of Figs. 4b and c were 17 and 25 μsec , respectively.

Although the ^{13}C sensitivity obtained with the PPT method is significantly less than that obtained with an optimized Hartmann-Hahn transfer, there are also a

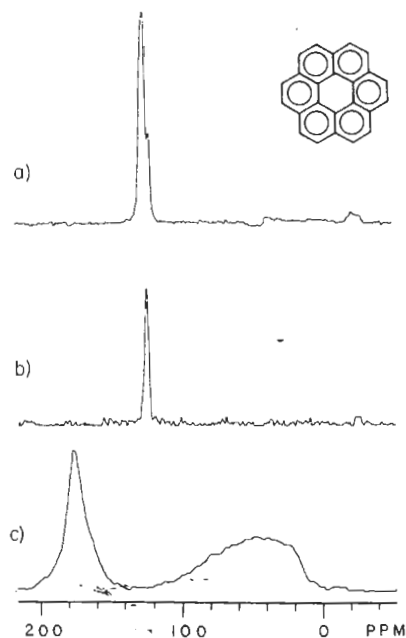


FIG. 4. ^{13}C NMR spectra of coronene. (a) The conventional CP-MAS spectrum; (b) the PPT spectrum with MAS, obtained from the same number of scans as in (a), but plotted at twice the absolute scale; (c) the PPT spectrum in the nonspinning mode. The τ_1 and τ_2 delays used in the PPT experiments were 17 and 25 μsec , respectively.

number of possible advantages in using the new sequence. It allows the study of the short-time behavior of the individual proton-carbon pairs in a polycrystalline solid, because magnetization is transferred from one proton to one ^{13}C only, analogous to the JBSLF experiment (8). However, sensitivity appears to be considerably better in the PPT experiment compared with the JBSLF experiment. Preliminary results show that it is also possible to distinguish between methylene and methine sites (12), in analogy to existing methods in liquid-state NMR (13, 14). Furthermore, the PPT method opens the way to the application in solid-state NMR of the many schemes for heteronuclear two-dimensional spectroscopy that are now commonly used for liquids (15-17). One would expect that the elimination of the proton-proton interaction during the times, τ_1 and τ_2 , e.g., by a WAHUA cycle (18) or a BLEW-12 cycle (19), would improve sensitivity by allowing the use of values for τ_1 and τ_2 that are closer to the optimal value, $(2D)^{-1}$. However, so far no large improvements have been obtained over the simple experiment sketched in Fig. 1.

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